Supporting Information for

Enhanced Stability and Efficiency for Photoelectrochemical Iodide Oxidation by Methyl Termination and Electrochemical Pt Deposition of n-Si Microwire Arrays

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Additional Experimental Details

Chemicals and Materials

All chemicals and materials were used as received unless noted otherwise. The hydriodic acid was unstabilized (Sigma Aldrich, 7.6 M, aq, 99.99%, or Alfa Aesar, 7.3 – 7.7 M, aq, ACS grade), except for the evaluation of planar Si samples for which stabilized hydriodic acid was used (Sigma Aldrich, 7.6 M, aq, 99.95%, < 1.5% hypophosphorous acid as stabilizer). All water was obtained from a Barnsted Nanopure system and had a resistivity >18 MΩ-cm. Nafion™ membranes were purchased from Ion Power (NR-212, 50.8 μm thick, equivalent weight of 1100 g of dry Nafion per mole sulfonic acid groups).

Materials Synthesis and Processing

Crystalline Si microwire arrays were grown on planar n-type Si(111) wafer substrates (University Wafer, Si(111) wafers, As-doped, 0.001-0.004 Ω-cm resistivity, 406.6 nm thermal oxide). Using photolithography, an array of holes (3 μm x 7 μm pitch) was patterned into the thermal oxide as a hexagonal pattern, and the holes were then filled with thermally evaporated Cu (EPSI, 6N). Si microwire arrays were grown on a ~2 cm x 3 cm chip at 1000 °C using flow rates of 500 sccm for H_2, 50 sccm for $SiCl_4$, and 0.6 – 1.0 sccm for PH_3 for 8 – 20 min. These growth conditions routinely produced microwires ~60 μm in height. After microwire growth, the samples were cooled to ~800 °C under H_2(g), cooled to ~200 °C under ambient pressure with a He headspace, and then removed from the reactor.

The samples were then cleaned via a standard procedure, involving a rinse with H_2O, an etch for 10 s with buffered HF(aq) (Transene, Inc.), followed immediately by rinsing with H_2O, two consecutive RCA2 cleans consisting of H_2O with equal parts HCl(12 M, aq) and H_2O_2(9.8 M, aq) (6:1:1 v/v/v) at 70 °C for 20 min. The sample was then immersed for 10 s in BHF(aq) followed immediately by rinsing with H_2O, 60 s in KOH(30 wt%, aq), and then 10 s in HF(~6 M, aq), followed immediately by rinsing with H_2O, drying under a stream of N_2(g), and subsequent thermal oxidation for 100 min at 1100 °C under a 4 L min^{-1} flow of O_2(g). Oxide "boots" were defined using polydimethylsiloxane (PDMS). PDMS was cast from a freshly prepared and degassed solution that contained toluene, PDMS, and an initiator (5 mL: 1 g: 0.1 g). This solution was spin cast on the microwire arrays for 30 s at 150 RPM, then for 30 s at 750 RPM, and then for 30 s at 1500 RPM. The PDMS was subsequently cured at 60 °C overnight in a vacuum oven followed by a final cure at 150 °C for 30 min on a hot plate. The oxide was removed from the exposed regions of the microwires using a 5 min soak in BHF(aq), followed immediately by rinsing with H_2O, a PDMS etch for ~5 sec that consisted of *N*-methyl-2-pyrrolidone with tetra-*n*-butylammonium fluoride (2.7 M, aq) (3:1, v/v), and then a PDMS etch that consisted of *N*,*N*-dimethylformamide with tetra-*n*-butylammonium fluoride (1.0 M, tetrahydrofuran) (1:1, v/v) until the PDMS was completely removed.

Surface Methylation

Immediately after etching samples with HF(~6 M, aq), samples were rinsed with H_2O, dried under a stream of N_2(g), and transferred to an N_2(g)-purged glovebox (<10 ppm O_2(g)). Samples were then immersed in a test tube containing chlorobenzene with saturated PCl_5 and freshly added benzoyl peroxide radical initiator, and heated at 90 °C for ~50 min to chlorinate the Si surface. The samples were rinsed ten times with neat chlorobenzene followed by ten times with neat tetrahydrofuran, dried briefly on a hot plate, rinsed three more times with neat tetrahydrofuran, and then transferred to another test tube containing a Grignard solution consisting of methylmagnesium chloride (~1 M) in tetrahydrofuran, which was used to methylate the Si surface via a reaction at ~55 °C for ~4 hr. The samples were then rinsed ten times with neat tetrahydrofuran followed by ten times with neat methanol, removed from the glovebox, rinsed three more times with neat methanol followed by three times with H_2O, dried under a stream of N_2(g), and stored under N_2(g) until use. Success of the two-step chlorination/alkylation reaction sequence in methylating atop sites on the silicon microwires is supported by large increases in water contact angle, X-ray photoelectron spectroscopy data, and electrode stability measurements (Figure S5).

Photoelectrode Fabrication and Photoelectrochemical Evaluation

The wafer was diced into several ~2.0 mm^2 pieces, and each piece was fashioned into an electrode of approximately the same area by lightly scratching the back side with In–Ga eutectic and using Ag paint to affix the eutectic-coated electrode onto a coiled, tinned Cu wire. The other end of the wire was then inserted into a glass tube and sealed using epoxy (Hysol 9460). The epoxy was left to cure overnight in a 60 °C oven and, if desired, Pt was then deposited on the electrode either electrochemically or by electron-beam evaporation (vide infra). Prior to electrochemical evaluation, each electrode was briefly etched in HF(~6 M, aq), and the current *versus* potential data were measured using a three-electrode configuration with a Si MW array working electrode, a Pt wire or small carbon-cloth quasi-reference electrode, and a Pt mesh or large carbon-cloth counter electrode. The electrolyte consisted of ~7.6 M HI(aq) that contained adventitious I_3^-, and air was continuously blown onto the cell for temperature control. The electrolyte was

rapidly stirred and was continuously purged with Ar(g). 1 Sun of simulated solar illumination at an intensity of 100 mW cm^{-2} was obtained from an ELH-type W–halogen lamp. The reversible formal potential for the aqueous I_3^-/I^- redox couple ($E(I_3^-/I^-)$) was determined using a Pt disk/button working electrode and a standard calomel electrode (KCl saturated) (SCE) as the reference electrode. The light intensity was determined using a calibrated Si photodiode (ThorLabs, Inc., FDS100) positioned at the location of the electrode, with the incident light passing through the borosilicate glass window of the electrochemical cell as well as through a thin path length of electrolyte. All reported current densities were referenced to the projected geometric area of the electrolyte contact to the electrode. Ultraviolet–visible electronic absorption spectra of the dissolved I_3^- were obtained using an HP 8452A diode-array spectrophotometer.

Electrochemical Deposition of Platinum

Electrodes were wetted with H_2O, etched for 15 s in HF(~6 M, aq), followed immediately by rinsing with H_2O, and then immersed in an aqueous solution of 5 mM K_2PtCl_4 (99.9%, Alfa Aesar) and 200 mM LiCl(aq). Using a three-electrode configuration with an SCE reference electrode and a Pt mesh counter electrode, the working electrode was held potentiostatically at –1.0 V *vs* SCE. The deposition was performed until at least 100 mC cm^{-2} of cathodic charge density had passed. The samples were then rinsed with H_2O and dried under a stream of N_2(g).

Electron-beam Evaporation of Platinum

Immediately after etching samples with HF(~6 M, aq), samples were rinsed with H_2O, dried under a stream of N_2(g), mounted onto a sample holder using Kapton tape affixed at the corners, placed into an evaporator (Denton Explorer) and positioned at an angle, set on planetary rotation, and pumped down to $< 1 \times 10^{-5}$ Torr. Pt was then deposited until the desired planar equivalent value was obtained on a calibrated quartz crystal microbalance.

Scanning Electron Microscopy with Energy Dispersive Spectroscopy

Imaging of Si microwire arrays during and after fabrication and processing, and when

affixed as electrodes, was performed on field-emission scanning-electron microscopes (Zeiss 1550VP). Validation that Pt was present on samples was determined using an energy-dispersive spectrometer with a silicon drift detector (Oxford X-Max^N).

Stability Analysis

Based on the data in Figure 5, the turnover number for net h^+ passed per Si atom was calculated to be ~900 as follows. A net integrated charge density of 837 C cm^{-2} was passed through the microwire array and because each microwire array contains one microwire per 7 x 7 μm unit cell, the average net charge passed per microwire was 410 μC = 4.25 nmol e^- and h^+. A ~50 μm tall microwire that is ~1.2 μm in diameter, representative of the microwires used in this study, has a volume of ~57 μm^3, which based on the density of crystalline Si (2.33 g mL^{-1} = 83 mmol Si cm^{-3}), yields ~4.7 pmol Si per microwire. Division of 4.25 nmol h^+ by ~4.7 pmol Si, yields the turnover number of h^+ per microwire. Since complete oxidation of each Si atom requires four holes, the observed photoanodic current cannot predominantly be ascribed to the oxidation of Si.

Additional Figures

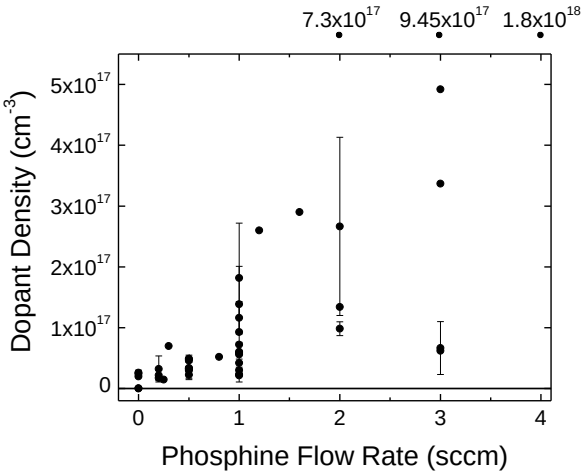

Figure S1. Mean (± standard deviation) dopant density data as a function of PH_3 flow rate for single n-type Si microwires taken from arrays grown at 1000 °C. Each point was obtained from a different microwire growth and error bars are shown when measurements were performed on multiple single microwires for a sample.

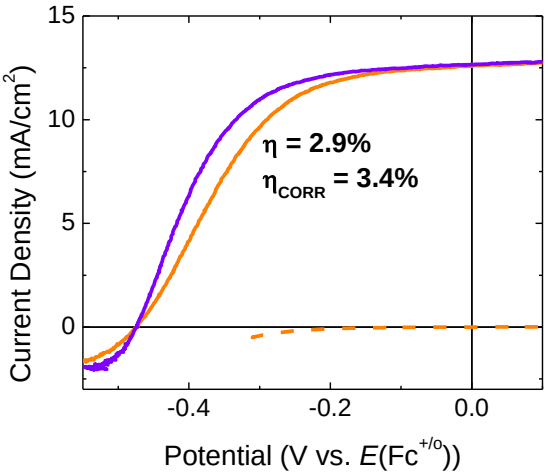

Figure S2. Three-electrode current density *versus* potential data recorded in the dark (dashed) or under 100 mW cm^{-2} of simulated AM1.5 G solar illumination (solid lines) provided by an ELH-type W-halogen bulb with a dichroic rear reflector for an n-type Si microwire array electrode immersed in Ar-purged 10 mM 1,1'-Me_2Fc^+, 100 mM Me_2Fc (where Me_2Fc is 1,1'-dimethylferrocene) in 1.0 M $LiClO_4$–CH_3OH. Also shown is the response after correcting for concentration overpotential (solid, purple; CORR),[45] and the calculated ideal regenerative-cell energy-conversion efficiency, η, for each.

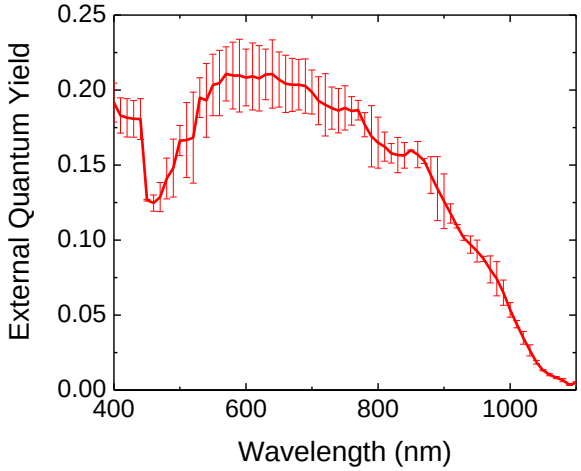

Figure S3. Mean (± standard deviation) normal-incidence spectral response data at 0 V vs. $E(Me_2Fc^{+/0})$ for two n-type Si microwire array electrode measurements in Ar-purged, 1 mM Me_2Fc^+, 100 mM Me_2Fc in 1.0 M $LiClO_4$–CH_3OH. The dip in the data at wavelengths less than 600 nm is due to solution absorption by Me_2Fc^+.[52]

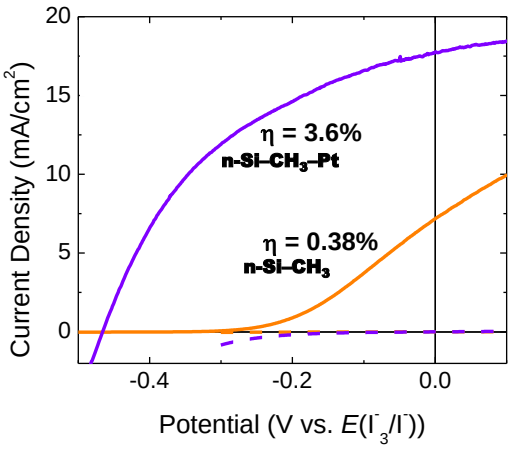

Figure S4. Three-electrode current density *versus* potential data recorded in the dark (dashed) or under 100 mW cm^{-2} of simulated AM1.5 G solar illumination (solid lines) for methylated n-type Si microwire array electrodes immersed in Ar-purged ~7.6 M HI(aq) containing adventitious I_3^-, with (purple) or without (orange) electrochemically deposited Pt. The purple data depict the behavior of the best-performing sample containing Pt, whereas the orange data represent a typical response in the absence of Pt, along with the calculated ideal regenerative-cell energy-conversion efficiency, η, for each. The reference electrode was a Pt wire poised at the Nernstian potential of the I_3^-/I^-(aq) redox couple.

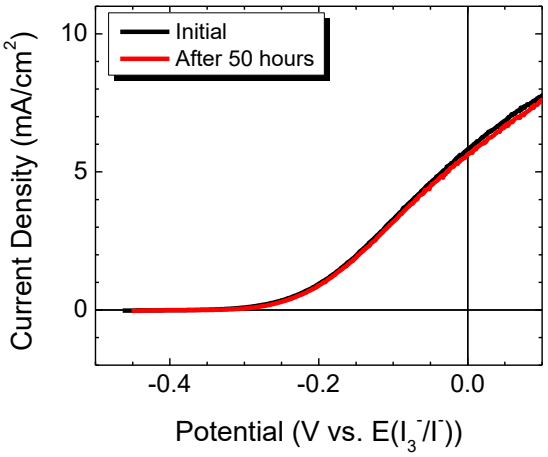

Figure S5. Three-electrode current density *versus* potential data recorded under 100 mW cm^{-2} of simulated AM1.5 G solar illumination for a methylated n-type Si microwire array electrode immersed in Ar-purged ~7.6 M HI(aq) containing adventitious I_3^-, initially (black) and after 50 h of continuous cyclic voltammetric operation (black) that passed a net total anodic charge density of 529 C cm^{-2}.

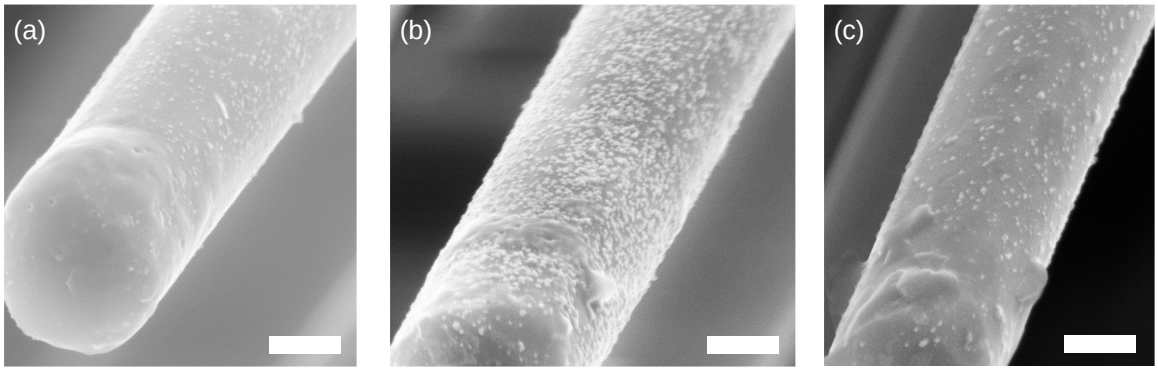

Figure S6. Representative scanning-electron micrograph images at 70,000 magnification (in lens detector) of nominally identical Si microwires obtained from the sample used in Figure 5 showing Pt nanoparticles (white dots) (a, b) before and (c) after photoelectrochemical analysis for 21 h, per the operation shown in Figure 5. Within variation between microwires no substantial change was observed in the microwire dimensions or in the shape or coverage of Pt, indicating that etching of Si and Pt was slow compared to oxidation of I^-(aq). All three scale bars are 500 nm.